

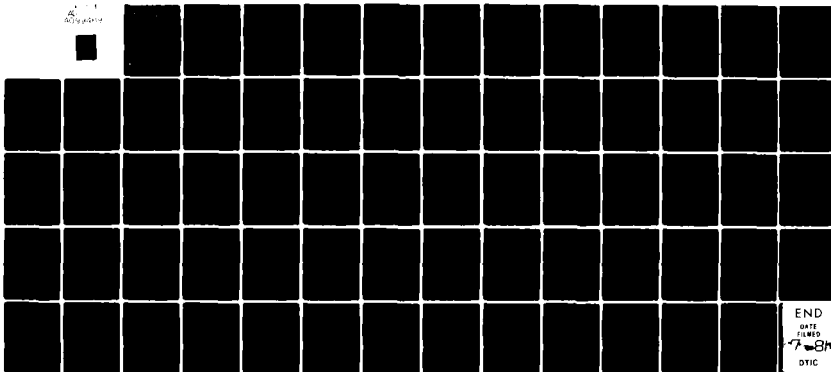
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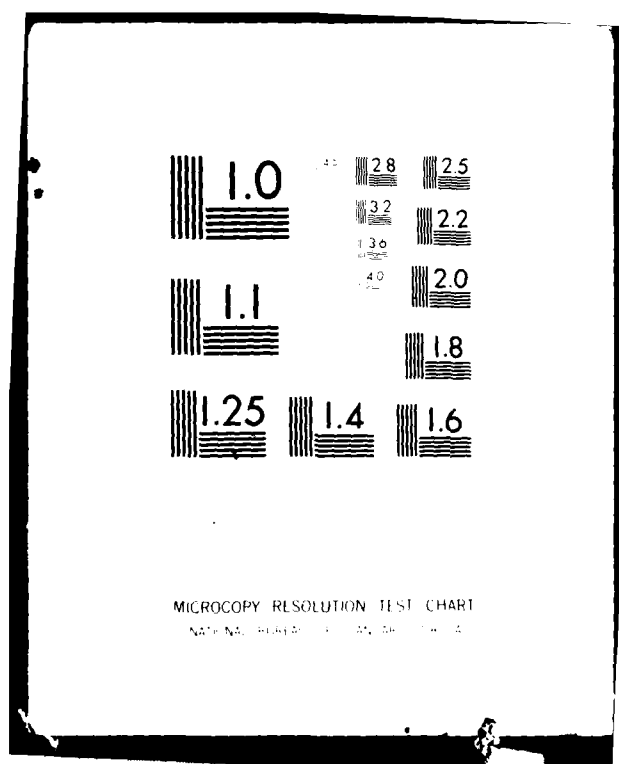
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U.S. Department
of Transportation
Federal Aviation
Administration

Disproportionation Reactions of Small Inorganic Radicals in the Context of Intermediate Complex Formation

Office of Environment
and Energy
Washington, D.C. 20591

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October 1980
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16. Abstract The reactions: $\text{HO}_2 + \text{NO} \rightarrow \text{HO} + \text{NO}_2$ $\text{CH}_3\text{O} + \text{NO} \rightarrow \text{CH}_3 + \text{NO}_2$ $\text{HO}_2 + \text{HO}_2 \rightarrow \text{H}_2\text{O}_2 + \text{O}_2$ $\text{HO}_2 + \text{OH} \rightarrow \text{H}_2\text{O} + \text{O}_2$ <p>have been analyzed within the framework of the formation of an intermediate complex. On the basis of RRKM calculations it is possible to infer that the first two reactions will not show any pressure dependence under stratospheric or tropospheric conditions. The observed small inverse temperature dependences are in accord with behavior of radical combination processes. However, despite exploration of wide range of parameters, it has not been possible to reproduce the observed pressure dependences for the last two processes through such calculations. The proper interpretation of the experiments and the nature of the H_2O_4 and H_2O_3 complexes are thus open to question.</p>			
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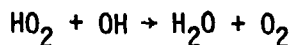
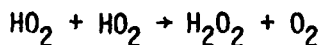
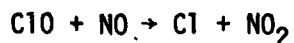
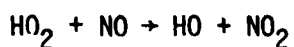
Disproportionation Reactions of Small Inorganic Radicals
in the Context of Intermediate Complex Formation

Wing Tsang

National Bureau of Standards
Chemical Kinetics Division
Center for Chemical Physics

Abstract

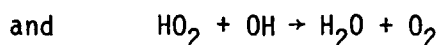
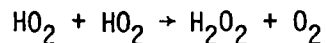
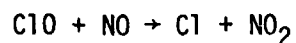
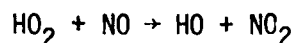
The reactions:



have been analyzed within the framework of the formation of an intermediate complex. On the basis of RRKM calculations it is possible to infer that the first two reactions will not show any pressure dependence under stratospheric or tropospheric conditions. The observed small inverse temperature dependences are in accord with behavior of radical combination processes. However, despite exploration of wide range of parameters, it has not been possible to reproduce the observed pressure dependences for the last two processes through such calculations. The proper interpretation of the experiments and the nature of the H_2O_4 and H_2O_3 complexes are thus open to question.

Introduction

This study is concerned with several reactions involving small inorganic radicals



These processes are of considerable importance in stratospheric and tropospheric pollution contexts (1). Of intrinsic interest is that these reactions involve the interaction of two radicals. Thus two reaction channels are possible, direct abstraction, or a process involving the formation of an intermediate complex. The present investigation treats all four processes in the framework of the latter mechanism. This is equivalent to considering these reactions as chemical activation processes and full use can be made of present day understanding of unimolecular decomposition processes (2,3). Specifically, with RRKM calculations* as an algorithm it is possible to connect information on the thermodynamics and kinetic stability of the proposed intermediate complexes with the experimental observations. Unfortunately, knowledge of the former is retarded by the instability of the complexes and the necessary information must in general be inferred. Nevertheless, in a suitably parameterized form such an analysis may be of value when fitted to experimental results in providing extrapolations and guidelines for future work. Alternatively, one can regard these calculations as a test of the applicability of the assumptions inherent in RRKM calculations.

* Quantum-statistical treatment of unimolecular processes developed by Rice, Ramsberger, Kassel and Marcus. See references 2 and 3.

Of particular concern is the fact that these systems are among the smallest to be treated in this manner.

This report will consist of three parts, first, a summary of existing experimental determinations, second, the required structural thermodynamic and kinetic data which are the basis for RRKM calculations and finally, the results of the calculations and its correspondence with experiments.

Experimental Results

The results of the most recent evaluation of the data on the four systems can be found in Appendix I (4). In Appendix Ib we have added results of some subsequent work. They do not change the recommendations from the earlier work. The important factors to be noted are:

- (a) the large volume of experimental data on these systems,
- (b) the most reliable and recommended results are those derived from direct measurements of reactants or products,
- (c) these experiments [b] are always carried out at low pressures,
- (d) the higher pressure results inevitably involve interpretation of complex mechanism; they must be regarded as much more uncertain,
- (e) the negative temperature dependence for the bimolecular process,
- (f) the pressure dependence of the HO_2 self-reaction, particularly at lower pressures and determined using direct methods; thus less subject to ambiguities, and
- (g) the possibility of complex formation of HO_2 with water and other substances.

Properties of Intermediate Complex

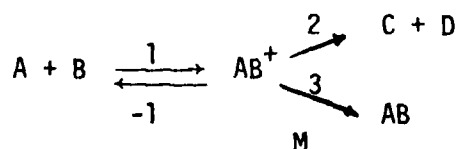
Thermodynamic and structural properties of the intermediate complex and reactants are summarized in Appendix II. As has been noted, there

are important uncertainties in these properties. Of major importance are the torsional frequencies for the OH groups in HO_2NO , H_2O_4 and H_2O_3 . We have spanned the range of possibilities by carrying out calculations for 100 cm^{-1} and 500 cm^{-1} values. It should be noted that for processes at 300 K, high frequency modes do not make significant contributions and thus uncertainties should be unimportant. The heats of formation of the four intermediate complexes as well as HO_2 are all uncertain but the numbers used here should span the entire range. It should be noted that we are assuming bent linear structures for H_2O_4 and H_2O_3 [as opposed to cyclic structures]. All thermodynamics and vibrational frequencies are estimated on this basis. If these compounds should have different structural forms the necessary estimate will be so uncertain that this type of calculation will be of questionable value.

The pertinent kinetic data are the Arrhenius rate parameters for unimolecular decomposition into products. Direct studies are unavailable. For bond breaking studies A-factors in the range of $10^{15}\text{--}10^{17}\text{ s}^{-1}$ should span all possibilities. The activation energy is simply the bond energy. The uncertainties in the enthalpies of formation of reactants and products from which the latter number is deduced has been noted earlier. The self reaction of HO_2 and its reaction with OH involve a more complicated mechanism for the decomposition of the intermediate complex. The transition state should be considerably tighter than for bond-breaking, hence a lower A-factor. There should also be a barrier for the reverse process. The range of possible variations is thus considerably larger than for bond breaking. On this basis the first tests must be to see whether a fit of the experimental results is possible with "reasonable" thermochemical and kinetic parameters.

RRKM Calculations

The detailed mechanism for reaction via an intermediate complex can be written as



The observed bimolecular rate is thus

$$k(\text{obs}) = k_1(k_2 + k_3M)/(k_{-1} + k_2 + k_3M)$$

where the subscripts, 1, -1, 2, 3 refer to association at ∞ pressure, specific rate for dissociation, specific rate for disproportionation and collisional stabilization respectively. Such a mechanism accounts in a very natural manner for any dependence of rate constants with pressure. However it should be noted that within the context of the strong collision hypothesis that will be used here such effects can only be observed in stratospheric contexts for a limited range of k_{-1} and k_2 .

Furthermore, from the subsequent calculations, it is readily established that k_{-1} and k_2 are very weakly dependent on pressure. On this basis one sees that as the disproportionation process (k_2) becomes more important than dissociation (k_{-1}), any pressure dependence will become weaker irrespective of the deactivation rate (k_3M). On the other hand third order behavior can only occur when the dissociation rate k_{-1} is larger than deactivation (k_3M) and if the latter is in turn larger than the disproportionation rate (k_2). Thus the observations of such behavior represent proof that the main reaction process involves formation of a stable complex.

The procedures used in carrying out RRKM calculations in the context of chemical activation experiments have been summarized in standard

texts (2,3). The required relations are, for the specific rate at energy E

$$k(E) = \alpha G^*(E-E_0)/h \cdot N(E) \cdot F$$

where α is the reaction degeneracy, E_0 is the critical energy, $G^*(E-E_0)$ is the sum of states of the transition state, $N(E)$ the density of states of the activated molecule and F a correction factor to take into account centrifugal effects. The latter is calculated following the formulation of Waage and Rabinovitch (5) and using a ratio of the moment of inertia (I^*/I , transition state/normal molecule) as derived by Forst (3) assuming a $1/r^6$ potential. The observed specific rates $k_2^1(E)$ and $k_1^1(E)$ are

$$k_2^1(E) = \frac{k_3^M \int_0^\infty \{k_2(E) F(E)/(k_2(E) + k_{-1}(E) + k_3^M)\} dE}{\int_0^\infty \{k_3^M F(E)/(k_2(E) + k_{-1}(E) + k_3^M)\} dE}$$

and an analogous relation for $k_1^1(E)$. $F(E)$ is the distribution function for the newly formed intermediate complex. Assuming thermalization of the complex, Rabinovitch and Diesen (6) derived a general expression in the form of

$$F(E) = G^*(E-E_0) e^{-E/RT} / N \quad E > E_0$$

where $G^*(E-E_0)$ is the sum of states of the transition state for the decomposition of the adduct and N is a normalization factor. Note that if thermalization is not attained, then the adduct can be at some alternative temperature, thus the temperature in the above relationship can also be regarded as an adjustable parameter.

The present calculations have been carried out on the basis of a direct count of the sum of vibrational states using the method of Stein

and Rabinovitch (7). Rotations are assumed to be classical. The density of states are calculated using the Whitten-Rabinovitch approximation. Validity of the calculational procedure was demonstrated by reproducing the results published by Hassler and Setser (8) on ethyl chloride. In the subsequent sections we propose to deal with each system individually.

(a) $\text{HO}_2 + \text{NO} \rightarrow \text{HO} + \text{NO}_2$. The two decomposition paths of the intermediate both involve bond cleavage into a polyatomic and a diatomic molecule. The A-factors should therefore be very close to each other. Since the details of the transition state are not of great importance as long as the correct A-factors are reproduced (2), it is clear that the reaction energy differences will control the branching ratio. Depending on the value of the heat of formation of the HO_2 radical the excess energy for disproportionation as compared to dissociation will be between 20 kJ to 41 kJ. This uncertainty is also manifested in the depth of the well for the $\text{HO}_2\text{-NO}$ complex with an added factor of about 12 kJ from possible errors in the heat of formation of the complex.

The transition state structures for these calculations are based on a parameterized version of Benson's restricted rotor (9) model. The physical picture is that of two radicals tumbling about each other. This motion is restricted when the fragments are too close and is expressed in a lowered moment of inertia. Since in the diatomic approximation the rotational barrier moves closer to the origin as the temperature is increased one expects an increase in "hindrance" at lower temperatures. For the present purposes we have simply added a multiplicative term in the expressions involving active rotations in the form of

$$\propto (T/300)^\beta$$

where α and β are constants which are adjusted so as to bring experimental results into conjunction with calculations. The only restriction is that α is less than 1 and β is negative. Such an approach represents a 2-parameter fit of the data and in analogous form has been used by Golden and colleagues (10) to fit results of many similar processes. In the present case we have the added complications of the uncertainties mentioned earlier.

Results of the RRKM calculations for the $\text{HO}_2 + \text{NO} \rightarrow \text{HO} + \text{NO}_2$ process are summarized in Appendix III. The procedure is to first carry out a calculation with a certain set of parameters and then to examine the results of systematic changes. Thus Appendix IIIa consider the effect of enthalpy changes, Appendix IIIb the effect of structural changes for the intermediate complex, Appendix IIIc the treatment of external rotations and Appendix IIId effects due to different A-factors. In all cases, by suitable choice of α and β , one can reproduce the experimental results. The A-factors required do not appear to be unreasonable. On the other hand the calculated lifetimes approach 10^{14} /sec in certain cases and one may well question the physical significance of such numbers. Generally the key factors are the much larger rates for disproportionation compared with those for dissociation. This is a direct result of the larger reaction exothermicity for the former and, as can be expected from the earlier discussion, leads to virtually a complete lack of pressure dependence. As expected, when the dissociation rate approaches the disproportionation rate there is an increasing pressure dependence. In the context of these calculations they are still rather small. Furthermore in order to attain these results the models that must be utilized are not very plausible. In one case we have chosen to treat the external

rotation about the figure axis to be active in the normal molecule and the transition state for the dissociation complex but inactive for the disproportionation situation. The other case is for widely different A-factors and is not what one would expect for such processes. Most of the specific rates are in the 10^{10} to 10^{12} sec^{-1} region. This is far above the strong collision quenching rate at atmospheric pressure. Thus even the small pressure effects are not expected to occur until pressures are in the tens of atmosphere or more. For weak collisions, transition pressures will be even higher. Finally, non-equilibration of the HO_2NO adduct should not seriously affect these results since a colder adduct will simply accentuate the importance of the disproportionation channel, while a hot adduct can lead to rates for disproportionation and dissociation that are closer to each other but will move the transition region to even higher pressure. The general conclusion must be that the observed rate for the $\text{HO}_2 + \text{NO}$ reaction is unlikely to exhibit pressure dependence over any range of stratospheric and tropospheric concern.

(b) $\text{ClO} + \text{NO} \rightarrow \text{Cl} + \text{NO}_2$. The general situation for this reaction is very similar to that for the $\text{HO}_2 + \text{NO}$ process. In the present case we have the disproportionation reaction going to form an atom and a polyatomic species while dissociation yields two diatomics. In order to fit the data, a difference in A-factors of about an order of magnitude is required (see Appendix IV). Thermodynamic and structural parameters are more certain inasmuch as the heats of formation of the reactants and products are well known. Thus the overall exothermicity of 35 kJ can be considered to be well established. As can be deduced from our earlier experience with HO_2NO , the uncertainty in the heat of formation in the context of a well depth of about 120 kJ should be unimportant. The results of RRKM calculations are summarized in Appendix IV and follow

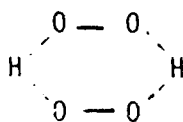
the general trends deduced for the HO_2NO system. The lower A-factor for disproportionation is apparently insufficient to compensate for the greater exothermicity. Thus disproportionation is favored and one has no reason in this case to expect any pressure dependence under stratospheric or tropospheric conditions.

(c) $\text{HO}_2 + \text{HO}_2 \rightarrow \text{H}_2\text{O}_2 + \text{O}_2$. The situation for this system is drastically different from that for the first two cases. First of all, the disproportionation reaction involves more complex decomposition processes than bond cleavage. Aside from the fact that this suggests a tighter transition state than for the latter, very little constraints can be placed on the A-factor. Thus it proved to be necessary to investigate a range of A-factors and activation energies for the decomposition of the complex into stable molecules. This has been done in Appendix Va. The heat of formation of the HO_2 radical represents a very important variable in these calculations. The recent number of $\Delta H_f(\text{HO}_2) \approx 0$ (11) at 300 K would remove the basis for the existence of any stable complex since it leads to the bond breaking process $\Delta H(\text{H}_2\text{O}_4 \rightarrow 2\text{HO}_2) = -4$ kJ at 300 K. We have accordingly carried out all calculation using the other high value of $\Delta H_f(\text{HO}_2) = 21$ kJ (12) at 300 K leading to a bond dissociation energy of close to 39 kJ. As it turned out this value is still too low for a satisfactory fit of the pressure dependence, since it leads to a very low density of states for H_2O_4 at the dissociation level and a correspondingly high specific rate. The results in Appendix Va do demonstrate that there is a range of acceptable rate parameters $[A_\infty, E_\infty]$ that can fit the measured rate constant at a given pressure (but not over all pressures). In Appendix Vb we considered the effect of uncertainties in the heat of formation of H_2O_4 . Clearly, in order to have any effect in reducing the specific

rate for dissociation this must be in the direction of higher values. It can be seen that a 21 kJ increase lowers the rate by an order of magnitude but is still too high if the pressure dependence is to be matched. Appendix Vc summarizes the results derived assuming a loose structure for the H_2O_4 complex. This involves assigning values of 100 cm^{-1} for the two OH torsional modes. Together with the stiff complex with a 450 cm^{-1} torsional frequency mode the present calculation should bracket all possibilities. Nevertheless specific rates remain orders of magnitude higher than the values required to reproduce the observed pressure dependence. The effects arising from the treatment of external rotations can be found in Appendix Vd. It can be seen that if we assume that the external rotation about the figure axis of H_2O_4 is active, while this motion for the transition state of the two decomposition paths remains, inactive, a reduction in $k(\text{diss})$ of a factor of 50 can be achieved. Nevertheless this is not sufficient. Note that if one makes all external rotations active, the calculated numbers become very similar to the situation where the external rotations are totally inactive. Finally in Appendix Ve we examine the situation where H_2O_4 is not equilibrated and assign an arbitrary "temperature" of 100 K to the newly formed molecule. A lowering of $k(\text{diss})$ by a factor of 5 is achieved. This is not sufficient for the present purposes. It will be noted that in making these trials we have carried them out in a cumulative fashion so that the final results [except for H_2O_4 enthalpy effect] represent the situation that most closely reproduces the experimental dependence. Nevertheless the pressure dependence is not obtained and indeed we are still close to 2 orders of magnitude in $k(\text{diss})$ away from the desired number.

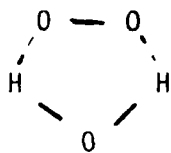
On this basis we conclude that there is no RRKM model that is capable of reproducing the observed pressure dependence. It should be

noted that the results of Thrush and coworkers (13) indicating termolecular behavior at a few torrs pressure calls into question the proposed stoichiometry of the reaction $2\text{HO}_2 \rightarrow \text{H}_2\text{O}_2 + \text{O}_2$ since it implies $k(\text{obs}) = k_1 k_3^M / (k_{-1})$ and thus $k_{-1} > k_3^M > k_2$. Furthermore since k_3^M is $\sim 2 \times 10^7/\text{sec}$ at 1 torr pressure, and $k_1 \sim 2 \times 10^9/\text{sec}$ this means that, in view of the termolecular behavior, k_{-1} must be of the order of $10^8/\text{sec}$. As can be seen from the calculation these numbers are not compatible. Note that k_1 and k_{-1} are related in a complicated manner through the equilibrium constants, density of states and transition state structure. Thus specifying one number places severe constraints on the other. Indeed, in the most naive interpretation, they are proportional to each other. In the present analysis we have placed primary emphasis on reproducing rate constants. In view of our inability to find a set of k_1 and $k(\text{diss})$ values that will do this it proved necessary to use a value of $k(\text{disp})$ that in the appropriate pressure ranges is greater than k_3^M . The termolecular dependence is thus lost even though the rate constants are now nearer the experimental. Overall, one suspects that this reaction is worthy of further experimental work. Thus direct experiments over the entire pressure range should prove to be extremely rewarding. It may well be that the complex is behaving in a non-RRKM manner. Alternatively, one is struck by the fact that the fundamental problem in the present calculations is due to the shallow well for the dissociation of the H_2O_4 complex. We have of course assumed the usual HOOOH structure. It could be that the problems encountered here arise from the fact that the thermodynamically more stable structure is that of a cyclic 6-membered ring



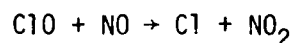
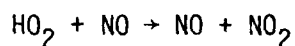
Unfortunately the kinetic and thermodynamic parameters for such a system are highly uncertain and while one can certainly fit the results, the increased number of adjustable parameters make conclusions highly suspect.

(d) $\text{HO}_2 + \text{OH} \rightarrow \text{H}_2\text{O} + \text{O}_2$. The general situation for this process is similar to the HO_2 self disproportionation reaction. There are uncertainties in the thermochemistry and there are no particular constraints on the rate parameters for the disproportionation reaction. Regardless of the heat of formation of HO_2 a thermodynamically stable complex can be formed with a well-depth for dissociation (into HO_2 and OH) of no less than 105 kJ. Results of RRKM calculations are summarized in Appendix VI. The tests that have been performed demonstrate, effects due to uncertainties in rate parameters for disproportionation processes, Appendix VIb, effects arising from treatment of external rotations, Appendix VIc, effects arising from uncertainty in the enthalpy of H_2O_3 , Appendix Vid, and effects arising from uncertainties in the vibrational frequencies of H_2O_3 . These calculations and the previous results demonstrate that the problems here are as before, the fast rate for dissociation, and it appears that only by a unnatural treatment of the external rotation can one approach the proper pressure dependence. As before, at any given pressure, the observed rate constants can be derived. It should be noted that the experimental pressure dependence for this reaction is considerably more uncertain than for the H_2O_4 self reaction and further experimental work would certainly be appropriate. Finally, the possibility of a cyclic intermediate complex which is more stable than the linear HOOOH structure would provide a very simple solution.

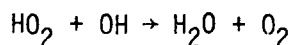
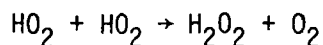


Summary

The results of these calculations demonstrate that regardless of reaction mechanism the processes



will follow bimolecular behavior across all pressure ranges. If the intermediate complex mechanism is assumed, this is brought about by the greater exothermicity of the disproportionation channel, making this under normal conditions the most important reaction. This has the practical effect of removing virtually all pressure dependence from the observed rate even when collisional deactivation becomes faster than disproportionation. The observed inverse temperature dependence is fully in line with observations involving other radical combination processes. The calculations for the reactions



are less certain. This is because it has not been possible to reproduce the observed pressure dependence. The situation is especially serious for the HO_2 self reaction. Two particular points should be noted. If $\Delta H_f(\text{HO}_2) = 0$ at 300 K, then there is no basis for talking about an intermediate complex mechanism with a HO_2OOH geometry since the dissociation process is in fact exothermic. Secondly if the observed termolecular behavior is correct, then the stoichiometry of the process cannot be that of H_2O_2 production.

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Appendix Ia: Summary of Experimental Results

CHEMICAL KINETICS DATA SURVEY
PREPARED AT CHEMICAL KINETICS DATA CENTER, NATIONAL BUREAU OF STANDARDS

Uncert. factor
at 298, unless
indicated

No.

Reaction/Reference

Temp,
Range/K

Reaction Rate Constant
M/cm³ molecule⁻¹ s⁻¹

9.20

NO + HCl₂ = NO₂ + HCl

ΔR (298) = -20 kJ/mol

NASA (1979) eval

200-300

$4.3 \times 10^{-12} \exp((200 \pm 200)/T)$

1.2

LEDA (1979) eval

230-425

$4.3 \times 10^{-12} \exp((200 \pm 200)/T)$

1.2

Zehnliser, Howard (1978)

230-400

$3.3 \times 10^{-12} \exp(254/T)$

Leu (1979)

270-425

$5.7 \times 10^{-12} \exp(130/T)$

Marrinen, Anderson (1978)

258

8.0×10^{-12}

Kaufman, Reimann (1978)

258

7.5×10^{-12}

Burrows, et al (1978)

298

8.2×10^{-12}

Howard, Evenson (1977)

256

$(8.1 \pm 1.5) \times 10^{-12}$

Hack, et al (1975)

258-670

$2.0 \times 10^{-11} \exp(-1200/T)$

Simoneit, Melicklen (1977)

245-328

$k/(k_{ref})^{0.5} = 6.4 \times 10^{-6} \exp(-700/T)$

(a) ref rxn: $2HCl_2 \rightarrow H_2O_2 + Cl_2$

(a)

Cox, Derwent (1975)

256

1.2×10^{-12}

Payne, Stief, Davis (1973)

300

3×10^{-13}

Glanzer, Troe (1975)

1350-1700

7.5×10^{-12}

The recommendation is based on Zehnliser and Howard (1978) and Leu (1979) and the room temperature determinations of Marrinen and Anderson (1978) and Kaufman and Reimann (1978) and the ratio determination by Burrows et al (1978) relative to $Cl_2 + H_2O_2$. The agreement is excellent

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- F. F. Hampson
June 1979

CHEMICAL KINETICS DATA SURVEY
PREPARED AT CHEMICAL KINETICS DATA CENTER, NATIONAL BUREAU OF STANDARDS

No.	Reaction/Reference	Temp. Range/K	Reaction Rate Constant k/cm ³ molecule ⁻¹ s ⁻¹	Uncert. Factor at 298K, notes
9.36	NO + ClO → NO ₂ + Cl		ΔH (298) = - 38 kJ/mol	
	NASA (1979) eval	200-300	7.8 x 10 ⁻¹² exp((250±100)/T)	1-25
	CODATA (1979) eval	227-415	3.5 x 10 ⁻¹² exp((210±100)/T)	1-25
	Leu, DeMore (1978)	227-415	5.7 x 10 ⁻¹² exp(296/T)	
	Watson, Ray (1979)	298	1.75 x 10 ⁻¹¹	
	Clyne, Watson (1974a)	298	1.7 x 10 ⁻¹¹	
	Watson (1977) review	220-298	8 x 10 ⁻¹² p(25/T)	
	Zahniser, Kaufman (1977)	230-298	k/k _{ref} = 1.52 ± 0.65 exp(373 ± 23/T) (a) k _{ref} = k(Cl + O ₃)	(a)

Changed from NASA 1010. The results of the three mass spectrometric studies (Clyne and Watson (1974a), Leu and DeMore (1978) and Watson and Ray (1979)) are in excellent agreement at 298 K. However, unless it can be shown that the value reported by Zahniser and Kaufman (1977) is in error, the preferred value at 298 K is taken to be the mean of all of these results. The magnitude of the temperature dependence reported by Leu and DeMore, and Zahniser and Kaufman is in good agreement. The Arrhenius expression was derived by taking the average of the two values of E/R and the pre-exponential A-factor was adjusted so that the expression yielded the preferred value of 1.8 x 10⁻¹¹ at 298 K.

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R. P. Hampson
June 1979

PREPARED AT CHEMICAL KINETICS DATA CENTER, NATIONAL BUREAU OF STANDARDS

No	Reaction/Reference	Temp Range/K	Reaction Rate Constant		Uncert. Factor at 298K, mol/cm ³
			k/cm ³ molecule ⁻¹ s ⁻¹	log ₁₀ k	
26.2°	H ₂ + H ₂ O ₂ → H ₂ O + H ₂ O		ΔH (298) = -140 kJ/mol		
	NASA (1979) eval	200-300	2.5 × 10 ⁻¹²		2
	CMData (1979) eval		Δ(E/R) = 0, -1245		
	Hamilton, LII (1977)	298	2.3 × 10 ⁻¹²		2
	Cox (1978)	258	2.5 × 10 ⁻¹²		
	Burrows, et al (1978)	273-338	3.8 × 10 ⁻¹⁴ exp(1245/T)		P = 1 atm
	Baulch, et al (1972) review	208	4.1 × 10 ⁻¹²		P = 2 torr
		300	3.3 × 10 ⁻¹²		

This is the room temperature value of Hamilton and LII (1977) and Cox (1978). Both studies found the rate constant to be sensitive to the presence of water vapor (at the torr level). There is preliminary evidence in the Cox study for a very strong negative temperature dependence (E/R = -1245K) although the data are very limited. However, there is evidence that the strong T dependence is not present at lower pressures. Thus, for the time being, E/R = 0, with a lower uncertainty bound of -1245K is recommended. Preliminary evidence of a pressure dependence (Burrows et al, 1978; Cox, 1978) would, if confirmed, require a further change in the recommendation. Recent measurements of the relevant rate constant ratios in a study by DeMore (1979) are consistent with both the water vapor and temperature effects cited by Cox.

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P. F. Hampson
June 1970

CHEMICAL KINETICS DATA SURVEY
PREPARED AT CHEMICAL KINETICS DATA CENTER, NATIONAL BUREAU OF STANDARDS

Reaction/Reference
Temp.
Range/K
Reaction Rate Constant
k/cm³molecule⁻¹s⁻¹
Uncertainty Factor
at 298K, notes

19.20	H ₂ + HCl → H ₂ + Cl ₂			ΔR (298) = -283 kJ/mol	
	NASA (1979) eval	200-300		4 × 10 ⁻¹¹ exp((0±250)/T)	2
	CODATA (1979) eval	258		3.5 × 10 ⁻¹¹	3
	Chang, Kaufman (1978)	295		2-3 × 10 ⁻¹¹	
	DeMore (1979)	258		~1 × 10 ⁻¹⁰	
	Back, et al (1978)	253		(3 ± 1) × 10 ⁻¹¹	
	Burrows, Harris, Thrush (1977)	293		5.1 × 10 ⁻¹¹	(a)
				(a) Based on k(H ₂ + H ₂ O ₂) = 8 × 10 ⁻¹³	
	Rochanadel, et al (1972)	300		2 × 10 ⁻¹⁰	
	DeMore, Tschukow-Roux (1974)	300		~1 × 10 ⁻¹⁰	

The recommended value is derived from the upper limit of Chang and Kaufman (1978), the measurement of Rack et al (1978), and the ratio measurement (relative to OH + H₂O₂) by Burrows et al (1977) and is within the experimental accuracy of all three studies, although it is not compatible with the value of 1-2 × 10⁻¹⁰ derived from rate constant ratios in steady state O₃ photolysis experiments by DeMore and Tschukow-Roux (1974) and DeMore (1979)

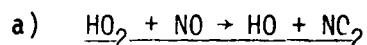
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R. F. Hampson
 June 1979

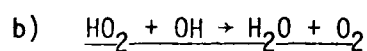
Appendix Ib: Recent work on reaction of interest



Glaschick-Schimpf et al 300 K $1.1 \times 10^{-11} \text{ cm}^3/\text{molecule-sec.}$

Glaschick-Schimpf, A Leiss, P. B. Monkhouse, U. Shurath, K. H.

Becker and E. H. Frank, Chemical Physics Letters 67, 218, 1979.



Hochanadel and Sworski 300 K, 1 atm $1.1 \times 10^{-10} \text{ cm}^3/\text{molecule-sec.}$

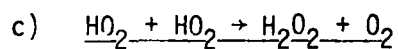
Lii, Gorse, Sauer and Gordon 308 K, 1200 Torr Ar $.99 \times 10^{-10} \text{ cm}^3/\text{molecule-sec.}$

C. J. Hochanadel and R. J. Sworski; Report on the Combustion Research

Contractors Meeting, Brookhaven, National Laboratory, October 9-11, 1979.

R. R. Lii, R. A. Gorse, M. C. Sauer and S. Gordon, J. Phys. Chem.,

84, 814, 1980.



Lii, Gorse, Sauer and Gordon 276-400 K $1.1 \times 10^{-13} \exp(1055/T)$
1200 Torr H_2

Thrush and Wilkinson 298 2 Torr He $2.9 \times 10^{-13} \text{ cm}^3/\text{molecule-sec.}$

3 Torr He $4.3 \times 10^{-13} \text{ cm}^3/\text{molecule-sec.}$

4 Torr He $5.5 \times 10^{-13} \text{ cm}^3/\text{molecule-sec.}$

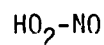
R. R. Lii, R. A. Gorse, M. C. Sauer, S. Gordon, J. Phys. Chem. 83,

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B. A. Thrush, and J. P. T. Wilkinson, Chem. Phys. Letter, 66,

441 (1979).

Appendix IIa: Structural Properties of Intermediate Complex



$$\Delta H_f(300) = -20 \text{ kJ/mol } (+ 30 \text{ kJ/mol})$$

CODATA data sheet, March 1979

Vibrational Frequencies (cm^{-1})

Bond Angle and Distances

3600 O-H stretch

O-O 1.48 Å

1600 N=O stretch

O-H .95 Å

1300 H-O bend

O-N 1.4 Å

860 O-N stretch

N=O 1.17 Å

800 O-O stretch

1.15°



650 O-N-O bend

110°



500 O-O-N bend

95°



500 [100] OH torsion

200 [100] NO torsion

Estimated from H_2O_3 , ClONO

Moment of Inertia

$$\begin{aligned} I_x I_y I_z &= 619 \times 10^{-117} \text{ cis} \\ &= 440 \times 10^{-117} \text{ trans} \end{aligned}$$

[] alternative frequency

ClONO

$$\Delta H_f(300) = 83.7 \text{ kJ/mol}$$



$$(\pm 20 \text{ kJ/mol})$$

Baulch et al., J. Phys.
Chem. Ref. Data 9, 295, 1980

Vibrational Frequencies (cm^{-1})

1713	N=O stretch
859	O-N stretch
646	O-NO bend
412	O-Cl stretch
260	Cl-ON bend
O-N	torsion

Bond Angle and Distances

N=O	1.17 Å
O-N	1.4 Å
O-Cl	1.7 Å
	115°
	111°

B. Janowski, H. D. Knauth and H. Martin, Berichte der Bunsen - Gesellschaft
Bd. 81, 1262, 1977.

Moment of Inertia

$$I_x I_y I_z = 1057 \times 10^{-117} \text{ gm cm}^2 \text{ trans}$$

$$= 463 \times 10^{-117} \text{ gm cm}^2 \text{ cis}$$



$$\Delta H_f(300) = -66.5 \text{ kJ/mol}$$

$$(\pm 8 \text{ kJ/mol})$$

P. S. Nangia and S. W. Benson,
J. Phys. Chem., 83, 1138 (1979).

Vibrational Frequencies (cm^{-1})

Bond Angle and Distances

3600 (2) O-H stretch

O-O 1.48 Å

1300 (2) OH bend

O-H .95 Å

800 (2) O-O stretch



500 (1) O-O-O bend



500 (2) [1001(2) OH torsion

J. L. Arnau and P. A. Giguere, J. Chem. Phys., 60, 270 (1974).

P. A. Giguere and I. D. Liu, J. AM. Chem. Soc., 74 6477 (1955).

Moment of Inertia

$$I_x I_y I_z = 133.1 \times 10^{-117} \text{ gm cm}^2$$

[] alternative frequency.



$$\Delta H_f(300) = 4.6 \text{ kJ/mol } (\pm 8 \text{ kJ/mol})$$

P. S. Nangia and S. W. Benson,
J. Phys. Chem., 83, 1138 (1979).

Vibrational Frequencies (cm^{-1})

Bond Angle and Distances

3600 (2) O-H stretch

1300 (2) OH bend

800 (3) O-O stretch

450 (2) O-O-O bend

O-O 1.48 Å

O-H .95 Å

 106°

500 (2)[100(2)] O-H torsion

 95°

100 (1) O-O torsion

J. L. Arnau and P. A. Giguere, J. Chem. Phys., 60, 270 (1974).

P. A. Giguere and I. D. Liu, J. Am. Chem. Soc., 77, 6477 (1955).

Moment of Inertia

$$I_x I_y I_z = 993 \times 10^{-117} \text{ gm cm}^2$$

[] alternative frequency.

Appendix IIb: Thermodynamic Properties of Species of Interest

OH

$$\Delta H_f(300) = 394 \text{ kJ/mol}$$

T	CP J/Mol.K	H-H(0) J/Mol.	S J/Mol.K	(G-H298)/T J/Mol.K
200	30.776	6196.0	171.478	-186.358
210	30.657	6503.2	172.978	-185.686
220	30.549	6809.2	174.402	-185.142
230	30.451	7114.2	175.758	-184.705
240	30.363	7418.3	177.053	-184.360
250	30.282	7721.5	178.291	-184.093
260	30.209	8023.9	179.478	-183.893
270	30.143	8325.7	180.617	-183.751
280	30.082	8626.8	181.713	-183.659
290	30.027	8927.3	182.767	-183.611
300	29.976	9227.4	183.785	-183.600

Molecular Properties are from JANAF Table (12).

NO

$$\Delta H_f(300) = 90.4 \text{ kJ/mol}$$

T	CP J/Mol.K	H-H(0) J/Mol.	S J/Mol.K	(G-H298)/T J/Mol.K
200	30.424	6241.6	198.636	-213.391
210	30.324	6545.3	200.118	-212.724
220	30.235	6848.1	201.526	-212.183
230	30.157	7150.1	202.868	-211.749
240	30.088	7451.3	204.150	-211.406
250	30.028	7751.8	205.377	-211.141
260	29.976	8051.9	206.554	-210.942
270	29.932	8351.4	207.685	-210.800
280	29.895	8650.5	208.772	-210.709
290	29.866	8949.3	209.821	-210.660
300	29.843	9247.9	210.833	-210.649

Molecular Properties are from JANAF Table (12).

C10

 $\Delta H_f(300) = 101.3 \text{ kJ/mol}$

T	CP J/Mol.K	H-H(0) J/Mol.	S J/Mol.K	(G-H298)/T J/Mol.K
200	29.811	5841.8	214.325	-229.366
210	29.962	6140.6	215.783	-228.685
220	30.124	6441.0	217.181	-228.131
230	30.294	6743.1	218.524	-227.684
240	30.470	7046.9	219.817	-227.329
250	30.652	7352.5	221.064	-227.054
260	30.836	7660.0	222.270	-226.847
270	31.023	7969.3	223.437	-226.699
280	31.210	8280.4	224.569	-226.603
290	31.396	8593.5	225.667	-226.552
300	31.581	8908.4	226.735	-226.540

Molecular Properties are from JANAF Table (12).

HO₂ $\Delta H_f(300) = 0 - 21 \text{ kJ/mol}$

T	CP J/Mol.K	H-H(0) J/Mol.	S J/Mol.K	(G-H298)/T J/Mol.K
200	33.485	6657.1	213.954	-230.675
210	33.564	6992.3	215.589	-229.918
220	33.658	7328.4	217.153	-229.302
230	33.767	7665.5	218.651	-228.807
240	33.891	8003.8	220.091	-228.414
250	34.030	8343.4	221.477	-228.109
260	34.183	8684.4	222.815	-227.880
270	34.350	9027.1	224.108	-227.716
280	34.530	9371.5	225.360	-227.610
290	34.721	9717.7	226.575	-227.553
300	34.923	10065.9	227.756	-227.541

Molecular Properties are from JANAF Table (12).



T	CP J/Mol.K	H-H(0) J/Mol.	S J/Mol.K	(G-H298)/T J/Mol.K
200	44.489	7220.7	239.093	-263.746
210	45.707	7671.7	241.293	-262.625
220	46.914	8134.8	243.447	-261.704
230	48.106	8609.9	245.559	-260.956
240	49.280	9096.8	247.631	-260.358
250	50.432	9595.4	249.666	-259.890
260	51.561	10105.4	251.666	-259.535
270	52.665	10626.6	253.633	-259.280
280	53.743	11158.6	255.568	-259.113
290	54.795	11701.3	257.472	-259.024
300	55.819	12254.4	259.347	-259.004

High frequency torsion.

T	CP J/Mol.K	H-H(0) J/Mol.	S J/Mol.K	(G-H298)/T J/Mol.K
200	54.186	9155.3	259.405	-287.788
210	54.918	9700.8	262.066	-286.501
220	55.660	10253.7	264.638	-285.449
230	56.407	10814.0	267.129	-284.598
240	57.158	11381.8	269.545	-283.921
250	57.910	11957.2	271.894	-283.393
260	58.661	12540.0	274.180	-282.995
270	59.408	13130.4	276.407	-282.710
280	60.151	13728.2	278.581	-282.524
290	60.887	14333.4	280.705	-282.425
300	61.616	14945.9	282.782	-282.402

Low frequency torsion.



T	CP J/Mol.K	H-H(0) J/Mol.	S J/Mol.K	(G-H298)/T J/Mol.K
200	57.629	8658.5	264.136	-296.257
210	59.316	9243.2	266.988	-294.796
220	60.976	9844.7	269.786	-293.596
230	62.604	10462.6	272.533	-292.620
240	64.198	11096.7	275.231	-291.840
250	65.753	11746.4	277.883	-291.229
260	67.268	12411.6	280.492	-290.766
270	68.743	13091.7	283.058	-290.433
280	70.175	13786.3	285.584	-290.215
290	71.565	14495.0	288.071	-290.098
300	72.913	15217.5	290.520	-290.071

High frequency torsion.

T	CP J/Mol.K	H-H(0) J/Mol.	S J/Mol.K	(G-H298)/T J/Mol.K
200	67.326	10593.1	284.448	-320.300
210	68.528	11272.3	287.762	-318.672
220	69.722	11963.6	290.977	-317.340
230	70.905	12666.7	294.102	-316.262
240	72.076	13381.7	297.145	-315.403
250	73.231	14108.2	300.111	-314.732
260	74.368	14846.2	303.005	-314.225
270	75.486	15595.5	305.833	-313.862
280	76.583	16355.9	308.598	-313.625
290	77.658	17127.1	311.304	-313.499
300	78.710	17908.9	313.955	-313.470

Low frequency torsion.

C1ONO

T	CP J/Mol.K	H-H(0) J/Mol.	S J/Mol.K	(G-H298)/T J/Mol.K
200	54.090	8717.9	267.988	-296.372
210	54.933	9263.0	270.647	-295.084
220	55.747	9816.4	273.221	-294.032
230	56.531	10377.8	275.717	-293.181
240	57.286	10946.9	278.139	-292.504
250	58.014	11523.5	280.492	-291.977
260	58.714	12107.1	282.781	-291.580
270	59.387	12697.7	285.010	-291.295
280	60.035	13294.8	287.182	-291.110
290	60.659	13898.3	289.299	-291.011
300	61.259	14507.9	291.366	-290.988

cis-form has entropy about 3.3 J/Mol.K lower but in view of other uncertainties should not effect results.

HO₂NO

T	CP J/Mol.K	H-H(0) J/Mol.	S J/Mol.K	(G-H298)/T J/Mol.K
200	54.247	9122.6	267.008	-295.833
210	55.137	9669.5	269.676	-294.525
220	56.046	10225.4	272.262	-293.454
230	56.968	10790.5	274.774	-292.588
240	57.897	11364.8	277.218	-291.897
250	58.827	11948.4	279.600	-291.357
260	59.756	12541.3	281.926	-290.950
270	60.679	13143.5	284.198	-290.658
280	61.594	13754.9	286.421	-290.467
290	62.497	14375.4	288.599	-290.365
300	63.388	15004.8	290.732	-290.342

High frequency torsion.

T	CP J/Mol.K	H-H(0) J/Mol.	S J/Mol.K	(G-H298)/T J/Mol.K
200	49.843	7858.9	252.224	-279.560
210	51.088	8363.6	254.686	-278.318
220	52.321	8880.6	257.091	-277.298
230	53.537	9409.9	259.444	-276.471
240	54.733	9951.3	261.748	-275.810
250	55.906	10504.5	264.006	-275.293
260	57.055	11069.4	266.221	-274.901
270	58.177	11645.5	268.396	-274.620
280	59.273	12232.8	270.531	-274.436
290	60.340	12830.9	272.630	-274.338
300	61.380	13439.5	274.693	-274.315

Low frequency torsion.

Appendix III: Inputs and Results on RRKM Calculations for
 $\text{HO}_2 + \text{NO} \rightarrow \text{HO} + \text{NO}_2$

Temperature 300 K	Mass 63.02	Collision diameter 5 Å			
	Normal Value	Transition State Dissociation		Transition State Disproportionation	
ΔE(kJs)		107.95		88.28	
Vibrations	9	4		4	
Frequencies cm ⁻¹	200, 500, 500 650, 800, 860 1300, 1600, 3600	1080, 1400, 1920 3400		760, 1360, 1680 3760	
Active (1-d)	0	2(1.5E-79)	(a)	2(1.7E-80)	(a)
Rotors (2-d)	0	1(2.5E-39)		1(6.6E-39)	
Inactive (1-d)	1(1.4E-39)	(a)	1(1.4E-39)	(a)	1(1.4E-39)
Rotors (2-d)	1(18E-39)		I ⁺ /I = 6.08		I ⁺ /I = 5.70
α		.084		.084	
β		-2.5		-2.5	
(a) \overline{I} (gm-cm ²)					
rotors					
k(diss) _∞ = 10 ^{15.9} exp(-12597/T)sec ⁻¹ k _∞ (assc) = 9.68					
k(disp) _∞ = 10 ^{15.9} exp(-10297/T)sec ⁻¹					
LGT[P(torr)]	LGT[k(diss)/sec]	LGT[k(disp)/sec]	LGT[k(stab)/sec]	LGT[k(obs)l/mol-sec]	
0	12.30	13.75	7.15	9.66	
1	12.30	13.75	8.15	9.66	
2	12.30	13.75	9.55	9.66	
3	12.30	13.75	10.15	9.66	
4	12.30	13.75	11.15	9.66	
5	12.31	13.75	12.15	9.66	
6	12.33	13.75	13.15	9.67	

Temperature* 200 K

	Normal Value	Transition State Dissociation		Transition State Disproportionation	
$\Delta E(\text{kJ})$		107.95		88.28	
Vibrations	9	4		4	
Frequencies cm^{-1}	200, 500, 500 650, 800, 860 1300, 1600, 3600	1080, 1400, 1920 3400		760, 1360, 1680 3760	
Active (1-d)	0	2(1.5E-79)	(a)	2(1.7E-80)	(a)
Rotors (2-d)	0	1(2.5E-39)		1(6.6E-39)	
Inactive (1-d)	1(1.4E-39) (a)	1(1.4E-39)	(a)	1(1.4E-39)	(a)
Rotors (2-d)	1(1.4E-39)	$I^+/I = 6.08$		$I^+/I = 5.70$	
α		.084		.084	
β		-2.5		-2.5	

(a) \overline{I} (gm-cm^2)
rotors

$$k(\text{diss})_{\infty} = 10^{16.3} \exp(-12885/T) \text{sec}^{-1} \quad k_{\infty}(\text{assc}) = 9.84$$

$$k(\text{disp})_{\infty} = 10^{16.25} \exp(-10522/T) \text{sec}^{-1}$$

LGT[P(torr)]	LGT[k(diss)/sec]	LGT[k(disp)/sec]	LGT[k(stab)/sec]	LGT[k(obs) ?/mol-sec]
0	12.44	14.06	7.24	9.83
1	12.44	14.06	8.24	9.83
2	12.44	14.06	9.24	9.83
3	12.44	14.06	10.24	9.83
4	12.44	14.06	11.24	9.83
5	12.44	14.06	12.24	9.83
6	12.46	14.07	13.23	9.83

* changed from previous trial.

Appendix IIIa: Effects of uncertainty in reaction energies

Temperature 300 K

	Normal Value	Transition State Dissociation	Transition State Disproportionation
$\Delta E(\text{kJ})$		128.9 [*]	109.2 [*]
Vibrations	9	4	4
Frequencies cm^{-1}	200, 500, 500 650, 800, 860 1300, 1600, 3600	1080, 1400, 1920 3400	760, 1360, 1680 3760
Active (1-d)	0	2(1.5E-79) (a)	2(1.7E-80) (a)
Rotors (2-d)	0	1(2.5E-39)	1(6.6E-39)
Inactive (1-d)	1(1.4E-39) (a)	1(1.4E-39) (a)	1(1.4E-39) (a)
Rotors (2-d)	1(18E-39)	$I^+/I = 6.43^*$	$I^+/I = 6.09^*$
α		.084	.084
β		-2.5	-2.5

(a) \overline{I} (gm-cm²)
rotors

$$k(\text{diss})_{\infty} = 10^{15.9} \exp(-15161/T) \text{sec}^{-1} \quad k_{\infty}(\text{assc}) = 9.70$$

$$k(\text{dispr})_{\infty} = 10^{15.15} \exp(-12815/T) \text{sec}^{-1}$$

LGT[P(torr)]	LGT[k(diss)/sec]	LGT[k(dispr)/sec]	LGT[k(stab)/sec]	LGT[k(obs)&/mol-sec]
0	11.88	13.31	7.15	9.69
1	11.88	13.31	8.15	9.69
2	11.88	13.31	9.15	9.69
3	11.88	13.31	10.15	9.69
4	11.89	13.31	11.15	9.69
5	11.89	13.32	12.15	9.69
6	11.93	13.33	13.15	9.69

* changed from previous trial.

Appendix IIIb: Effects arising from uncertainties in
vibrational frequency patterns for HO₂NO

1) Temperature 300 K

	Normal Value	Transition State Dissociation	Transition State Disproportionation
$\Delta E(\text{kJ})$		128.9	109.2
Vibrations	9	4	4
Frequencies cm^{-1}	100, 100, 500* 650, 800, 860 1300, 1600, 3600	1080, 1400, 1920 3400	760, 1360, 1680 3760
Active (1-d)	0	2(1.5E-79) (a)	2(1.7E-80) (a)
Rotors (2-d)	0	1(2.5E-39)	1(6.6E-39)
Inactive (1-d)	1(1.4E-39) (a)	1(1.4E-39) (a)	1(1.4E-39) (a)
Rotors (2-d)	1(18E-39)	I ⁺ /I = 6.43	I ⁺ /I = 6.09
α		.084	.084
B		-2.5	-2.5

(a) \tilde{I} (qm-cm²)
rotors

$$k(\text{diss})_{\infty} = 10^{14.7} \exp(-14945/T) \text{sec}^{-1} \quad k_{\infty}(\text{assc}) = 9.69$$

$$k(\text{disp})_{\infty} = 10^{14.65} \exp(-12598/T) \text{sec}^{-1}$$

LGT[P(torr)]	LGT[k(diss)/sec]	LGT[k(disp)/sec]	LGT[k(stab)/sec]	LGT[k(obs)/mol-sec]
0	10.62	12.05	7.15	9.67
1	10.62	12.05	8.15	9.67
2	10.62	12.05	9.15	9.67
3	10.62	12.05	10.15	9.67
4	10.67	12.07	11.15	9.68
5	10.69	12.09	12.15	9.68
6	10.74	12.10	13.15	9.69

* changed from previous trial.

2) Temperature 300 K

	Normal Value	Transition State Dissociation	Transition State Disproportionation
$\Delta E(\text{KJs})$		128.96	88.3*
Vibrations	9	4	4
Frequencies cm^{-1}	100, 100, 500 650, 800, 860 1300, 1600, 3600	1080, 1400, 1920 3400	760, 1360, 1680 3760
Active (1-d)	0	2(1.5E-79) (a)	2(1.7E-80) (a)
Rotors (2-d)	0	1(2.5E-39)	1(6.6E-39)
Inactive (1-d)	1(1.4E-39) (a)	1(1.4E-39) (a)	1(1.4E-39) (a)
Rotors (2-d)	1(18E-39)	$I^+/I = 6.43$	$I^+/I = 5.70^*$
α		.04	.04
β		-2.5	-2.5

(a) \overline{I} (gm-cm²)
rotors

$$k(\text{diss})_{\infty} = 10^{14.7} \exp(-14945/T) \text{sec}^{-1} \quad k_{\infty}(\text{assc}) = 9.69$$

$$k(\text{disp})_{\infty} = 10^{14.6} \exp(-10080/T) \text{sec}^{-1}$$

LGT[P(torr)]	LGT[k(diss)/sec]	LGT[k(disp)/sec]	LGT[k(stab)/sec]	LGT[k(obs)l/mol-sec]
0	10.71	12.95	7.15	9.69
1	10.71	12.95	8.15	9.69
2	10.71	12.95	9.15	9.69
3	10.71	12.95	10.15	9.69
4	10.71	12.95	11.15	9.69
5	10.71	12.95	12.15	9.69
6	10.74	12.95	13.15	9.69

* changed from previous trial.

3) Temperature 300 K

	Normal Value	Transition State Dissociation	Transition State Disproportionation
$\Delta E(\text{KJs})$		107.9*	88.3
Vibrations	9	4	4
Frequencies cm^{-1}	100, 100, 500 650, 800, 860 1300, 1600, 3600	1080, 1400, 1920 3400	760, 1360, 1680 3760
Active (1-d)	0	2(1.5E-79) (a)	2(1.7E-80) (a)
Rotors (2-d)	0	1(2.5E-39)	1(6.6E-39)
Inactive (1-d)	1(1.4E-39) (a)	1(1.4E-39) (a)	1(1.4E-39) (a)
Rotors (2-d)	1(18E-39)	$I^+/I = 6.08$ *	$I^+/I = 5.70$
α		.042	.042
β		-2.5	-2.5

(a) \overline{I} (gm-cm^2)
rotors

$$k(\text{diss})_{\infty} = 10^{14.7} \exp(-12416/T) \text{sec}^{-1} \quad k_{\infty}(\text{assc}) = 9.69$$

$$k(\text{disp})_{\infty} = 10^{14.65} \exp(-10080/T) \text{sec}^{-1}$$

LGT[P(torr)]	LGT[k(diss)/sec]	LGT[k(disp)/sec]	LGT[k(stab)/sec]	LGT[k(obs)l/mol-sec]
0	11.07	12.51	7.15	9.67
1	11.07	12.51	8.15	9.67
2	11.07	12.51	9.15	9.67
3	11.07	12.51	10.15	9.67
4	11.07	12.51	11.15	9.67
5	11.11	12.53	12.15	9.68
6	11.17	12.55	13.15	9.69

* changed from previous trial.

Appendix IIIc: Effects arising from treatment of external rotation
about figure axis

1) Temperature 300 K

	Normal Value	Transition State Dissociation	Transition State Disproportionation
$\Delta E(kJs)$		128.9*	109.2*
Vibrations	9	4	4
Frequencies cm ⁻¹	100, 100, 500 650, 800, 860 1300, 1600, 3600	1080, 1400, 1920 3400	760, 1360, 1680 3760
Active (1-d)	1(1.4E-39)* (a)	2(1.5E-79) (a)	2(1.7E-80) (a)
Rotors (2-d)	0	1(2.5E-39)	1(6.6E-39)
Inactive (1-d)	0 *	1(1.4E-39) (a)	1(1.4E-39) (a)
Rotors (2-d)	1(18E-39) (a)	I ⁺ /I = 6.43*	I ⁺ /I = 6.09*
α		.04	.04
β		-2.5	-2.5

(a) \overline{I} (gm-cm²)
rotors

$$k(\text{diss})_{\infty} = 10^{14.7} \exp(-14945/T) \text{sec}^{-1} \quad k_{\infty}(\text{assc}) = 9.69$$

$$k(\text{disp})_{\infty} = 10^{14.65} \exp(-12598/T) \text{sec}^{-1}$$

LGT[P(torr)]	LGT[k(diss)/sec]	LGT[k(disp)/sec]	LGT[k(stab)/sec]	LGT[k(obs)l/mol-sec]
0	8.91	10.34	7.15	9.67
1	8.91	10.34	8.15	9.67
2	8.92	10.34	9.15	9.68
3	8.96	10.36	10.15	9.68
4	9.02	10.38	11.15	9.69
5	9.04	10.39	12.15	9.69
6	9.04	10.39	13.15	9.69

* changed from previous trial.

2) Temperature 300 K

	Normal Value	Transition State Dissociation	Transition State Disproportionation
$\Delta E(\text{kJ})$		128.9	109.2
Vibrations	9	4	4
Frequencies cm^{-1}	100, 100, 500 650, 800, 860 1300, 1600, 3600	1080, 1400, 1920 3400	760, 1360, 1680 3760
Active (1-d)	1(1.4E-39) (a)	3(2.1E-118)* (a)	2(1.7E-80) (a)
Rotors (2-d)	0	1(2.5E-39)	1(6.6E-39)
Inactive (1-d)	0 (a)	0 *	1(1.4E-39) (a)
Rotors (2-d)	1(18E-39)	$I^+/I = 6.43$	$I^+/I = 6.09$
α		.08*	.08*
β		-2.5	-2.5

(a) \overline{I} (gm-cm²)
rotors

$$k(\text{diss})_{\infty} = 10^{15.0} \exp(-14945/T) \text{sec}^{-1} \quad k_{\infty}(\text{assc}) = 9.99$$

$$k(\text{disp})_{\infty} = 10^{15.0} \exp(-12599/T) \text{sec}^{-1}$$

LGT[P(torr)]	LGT[k(diss)/sec]	LGT[k(disp)/sec]	LGT[k(stab)/sec]	LGT[k(obs)l/mol-sec]
0	10.70	10.63	7.15	9.65
1	10.70	10.63	8.15	9.65
2	10.70	10.63	9.15	9.66
3	10.74	10.64	10.15	9.70
4	10.87	10.68	11.15	9.85
5	10.99	10.72	12.15	9.96
6	11.02	10.73	13.15	9.99

* changed from previous trial.

3) Temperature 300 K

	Normal Value	Transition State Dissociation	Transition State Disproportionation
$\Delta E(\text{kJ})$		128.9	109.2
Vibrations	9	4	4
Frequencies cm^{-1}	100, 100, 500 650, 800, 860 1300, 1600, 3600	1080, 1400, 1920 3400	760, 1360, 1680 3760
Active (1-d)	1(1.4E-39) (a)	3(2.1E-118) (a)	3(4E-119)* (a)
Rotors (2-d)	0	1(2.5E-39)	1(6.6E-39)
Inactive (1-d)	0 (a)	0 (a)	0 *
Rotors (2-d)	1(18E-39)	$I^+/I = 6.43$	$I^+/I = 6.09$
α		.04*	.04*
β		-2.5	-2.5
(a) \overline{I} (gm-cm ²) rotors			

$$k(\text{diss})_{\infty} = 10^{14.7} \exp(-14945/T) \text{sec}^{-1} \quad k_{\infty}(\text{assc}) = 9.69$$

$$k(\text{disp})_{\infty} = 10^{14.65} \exp(-12599/T) \text{sec}^{-1}$$

LGT[P(torr)]	LGT[k(diss)/sec]	LGT[k(disp)/sec]	LGT[k(stab)/sec]	LGT[k(obs) l/mol-sec]
0	10.56	12.10	7.15	9.68
1	10.56	12.10	8.15	9.68
2	10.56	12.10	9.15	9.68
3	10.56	12.10	10.15	9.68
4	10.57	12.10	11.15	9.68
5	10.64	12.13	12.15	9.68
6	10.70	12.15	13.15	9.68

* changed from previous trial.

Appendix IIId: Effects of large differential in A-factor

Temperature 300 K

	Normal Value	Transition State Dissociation	Transition State Disproportionation
$\Delta E(\text{kJ})$		107.95*	88.3*
Vibrations	9	4	4
Frequencies cm^{-1}	100, 100, 500 650, 800, 860 1300, 1600, 3600	1080, 1400, 1920 3400	760, 1360, 1680 3760
Active (1-d)	0	2(1.5E-79)* (a)	2(1.7E-80)* (a)
Rotors (2-d)	0	1(2.5E-39)	1(6.6E-39)
Inactive (1-d)	1(1.4E-39)* (a)	1(1.4E-39)* (a)	1(1.4E-39)* (a)
Rotors (2-d)	1(18E-39)	$I^+/I = 6.08^*$	$I^+/I = 5.70^*$
α		.11	.011
β		-2.5	-2.5

(a) \overline{I} (gm-cm^2)
rotors

$$k(\text{diss})_{\infty} = 10^{16} \exp(-12643/T) \text{sec}^{-1} \quad k_{\infty}(\text{assc}) = 9.80$$

$$k(\text{disp})_{\infty} = 10^{15} \exp(-10297/T) \text{sec}^{-1}$$

LGT[P(torr)]	LGT[k(diss)/sec]	LGT[k(disp)/sec]	LGT[k(stab)/sec]	LGT[k(obs)l/mol-sec]
0	12.37	12.85	7.15	9.67
1	12.37	12.85	8.15	9.67
2	12.37	12.85	9.15	9.67
3	12.37	12.85	10.15	9.67
4	12.37	12.85	11.15	9.67
5	12.40	12.86	12.15	9.69
6	12.47	12.86	13.15	9.74

* changed from previous trial.

Appendix IV: Inputs and Results for RRKM Calculation for
 $\text{ClO} + \text{NO} \rightarrow \text{Cl} + \text{NO}_2$

Temperature 300 K Mass 81.5 Collision diameter 5 Å

	Normal Value	Transition State Dissociation	Transition State Disproportionation
$\Delta E(\text{kJ})$		105.4	67.8
Vibrations	6	2	3
Frequencies cm^{-1}	100, 260, 412 646, 859, 1713	880, 1900	760, 1360,
Active (1-d)	0	3(9E-117)	0
Rotors (2-d)	0	0	1(5.5E-39)
Inactive (1-d)	1(1.28E-39) (a)	1(1.28E-39) (a)	1(1.28E-39)
Rotors (2-d)	1(28E-39)	$I^+/I = 6.01$	$I^+/I = 5.19$
α		.12	.5
β		-2	-2

(a) \overline{I} (gm-cm²)
rotors

$$k(\text{diss})_{\infty} = 10^{15.4} \exp(-12220/T) \text{sec}^{-1} \quad k_{\infty}(\text{assc}) = 10.2$$

$$k(\text{disp})_{\infty} = 10^{14.3} \exp(-7551/T)$$

LGT[P(torr)]	LGT[k(diss)/sec]	LGT[k(disp)/sec]	LGT[k(stab)/sec]	LGT[k(obs)l/mol-sec]
0	12.14	12.86	7.32	10.13
1	12.14	12.86	8.32	10.13
2	12.14	12.86	9.32	10.13
3	12.14	12.86	10.32	10.13
4	12.15	12.86	11.32	10.13
5	12.16	12.86	12.32	10.14
6	12.19	12.87	13.32	10.18

Temperature* 200 K

	Normal Value	Transition State Dissociation	Transition State Disproportionation
$\Delta E(\text{kJ})$		105.4	67.8
Vibrations	6	2	3
Frequencies cm^{-1}	100, 260, 412 646, 859, 1713	880, 1900	760, 1360, 1680
Active (1-d)	0	3(9E-117) (a)	0
Rotors (2-d)	0	0	1(5.5E-39) (a)
Inactive (1-d)	1(1.28-39) (a)	1(1.28E-39) (a)	1(1.28E-39)(a)
Rotors (2-d)	1(28E-39)	$I^+/I = 6.88$	$I^+/I = 5.94$
α		.12	.5
β		-2	-2

(a) \overline{I} (gm-cm^2)
rotors

$$k(\text{diss})_{\infty} = 10^{15.8} \exp(-12482/T) \text{sec}^{-1} \quad k_{\infty}(\text{assc}) = 10.49$$

$$k(\text{disp})_{\infty} = 10^{14.8} \exp(-7851/T)$$

LGT[P(torr)]	LGT[k(diss)/sec]	LGT[k(disp)/sec]	LGT[k(stab)/sec]	LGT[k(obs)l/mol-sec]
0	12.25	13.15	7.40	10.44
1	12.25	13.15	8.40	10.44
2	12.25	13.15	9.40	10.44
3	12.25	13.15	10.40	10.44
4	12.25	13.15	11.40	10.44
5	12.25	13.15	12.40	10.44
6	12.28	13.15	13.40	10.47

* changed from previous trial.

Appendix IVa: Effects arising from uncertainties C10NO heat of formation

Temperature* 300 K

	Normal Value	Transition State Dissociation	Transition State Disproportionation
$\Delta E(\text{kJ})$		126.36*	88.70*
Vibrations	6	2	3
Frequencies cm^{-1}	100, 260, 412 646, 859, 1713	880, 1900	760, 1360, 1680
Active (1-d)	0	3(9E-117) (a)	0
Rotors (2-d)	0	0	1(5.5E-39) (a)
Inactive (1-d)	1(1.28-39) (a)	1(1.28E-39) (a)	1(1.28E-39) (a)
Rotors (2-d)	1(28E-39)	1 ⁺ /I = 6.37*	1 ⁺ /I = 5.66*
α		.12	.5
β		-2	-2

(a) \overline{I} (gm-cm²)
rotors

$$k(\text{diss})_{\infty} = 10^{15.4} \exp(-14738/T) \text{sec}^{-1} \quad k_{\infty}(\text{assc}) = 10.23$$

$$k(\text{disp})_{\infty} = 10^{14.3} \exp(-10068/T)$$

LGT[P(torr)]	LGT[k(diss)/sec]	LGT[k(disp)/sec]	LGT[k(stab)/sec]	LGT[k(obs)l/mol-sec]
0	11.82	12.51	7.32	10.15
1	11.82	12.51	8.32	10.15
2	11.82	12.51	9.32	10.15
3	11.82	12.51	10.32	10.15
4	11.82	12.51	11.32	10.15
5	11.84	12.52	12.32	10.17
6	11.88	12.52	13.32	10.21

* changed from previous trial.

Appendix IVb: Effect of varying treatment of external rotations about
figure axis

1) Temperature 300 K

	Normal Value	Transition State Dissociation	Transition State Disproportionation
$\Delta E(\text{kJ/s})$		105.4*	67.8*
Vibrations	6	2	3
Frequencies cm^{-1}	100, 260, 412 646, 859, 1713	880, 1900	760, 1360, 1680
Active (1-d)	1(1.28E-39)* (a)	3(9E-117) (a)	0
Rotors (2-d)	0	0	1(5.5E-39) (a)
Inactive (1-d)	0* (a)	1(1.28E-39) (a)	1(1.28E-39) (a)
Rotors (2-d)	1(28E-39)	$I^+/I = 6.01^*$	$I^+/I = 5.19^*$
α		.12	.5
β		-2	-2

(a) \overline{I} (gm-cm²)
rotors

$$k(\text{diss})_{\infty} = 10^{15.35} \exp(-12220/T) \quad k_{\infty}(\text{assc}) = 10.20$$

$$k(\text{disp})_{\infty} = 10^{14.3} \exp(-7551/T)$$

LGT[P(torr)]	LGT[k(diss)/sec]	LGT[k(disp)/sec]	LGT[k(stab)/sec]	LGT[k(obs)l/mol-sec]
0	10.44	11.16	7.32	10.13
1	10.44	11.16	8.32	10.13
2	10.44	11.16	9.32	10.13
3	10.44	11.16	10.32	10.14
4	10.47	11.17	11.32	10.17
5	10.50	11.17	12.32	10.20
6	10.50	11.17	13.32	10.20

* changed from previous trial.

2) Temperature 300 K

	Normal Value	Transition State Dissociation	Transition State Disproportionation
$\Delta E(\text{kJ})$		105.4	67.8
Vibrations	6	2	3
Frequencies cm^{-1}	100, 260, 412 646, 859, 1713	880, 1900	760, 1360, 1680
Active (1-d)	1(1.28E-39) (a)	4(11.52E-156)* (a)	1(1.28E-39)* (a)
Rotors (2-d)	0	0	0
Inactive (1-d)	0	0*	0
Rotors (2-d)	1(28E-39) (a)	$I^+/I = 6.01$	$I^+/I = 5.33$
α		.12	.5
β		-2	-2

(a) \overline{I} (gm-cm²)
rotors

$$k(\text{diss})_{\infty} = 10^{15.35} \exp(-12220/T) \quad k_{\infty}(\text{assc}) = 10.20$$

$$k(\text{disp})_{\infty} = 10^{14.3} \exp(-7550/T)$$

LGT[P(torr)]	LGT[k(diss)/sec]	LGT[k(disp)/sec]	LGT[k(stab)/sec]	LGT[k(obs)l/mol-sec]
0	12.04	12.90	7.32	10.15
1	12.04	12.90	8.32	10.15
2	12.04	12.90	9.32	10.15
3	12.04	12.90	10.32	10.15
4	12.04	12.90	11.32	10.15
5	12.05	12.90	12.32	10.16
6	12.09	12.91	13.32	10.19

* changed from previous trial.

Appendix V: Inputs and Results on RRKM calculations for
 $\text{HO}_2 + \text{HO}_2 \rightarrow \text{H}_2\text{O}_4$

Temperature 300 K Mass 66.016 Collision diameter 5 Å

	Normal Value	Transition State Dissociation	Transition State Disproportionation
$\Delta E(\text{kJ})$		34.7	7.95
Vibrations	12	6	11
Frequencies cm ⁻¹	100, 450, 450, 500 500, 800, 800, 800 1300, 1300, 3600 3600	1120, 1120, 1360 1360, 3400, 3400	200, 200, 500, 500 700, 800, 800, 1300 1300, 3600, 3600
Active (1-d)	0	1(.5E-40) (a)	0
Rotors (2-d)	0	2(6.25E-78)	
Inactive (1-d)	1(6E-39)	(a) 1(6E-39) (a)	1(6E-39)
Rotors (2-d)	1(13E-39)	1 ⁺ /I = 4.28	1(13E-39)
α		.015	1
β		-2	0

(a) \overline{I} (gm-cm²)
rotors

$$k(\text{diss})_{\infty} = 10^{15.7} \exp(-3923/T) \quad k_{\infty}(\text{assc}) = 9.28$$

$$k(\text{disp})_{\infty} = 10^{13.1} \exp(-1222/T)$$

LGT[P(torr)]	LGT[k(diss)/sec]	LGT[k(disp)/sec]	LGT[k(stab)/sec]	LGT[k(obs)l/mol-sec]
0	13.71	12.55	7.16	8.09
1	13.71	12.55	8.16	8.09
2	13.71	12.55	9.16	8.09
3	13.71	12.55	10.16	8.09
4	13.71	12.55	11.16	8.10
5	13.53	12.55	12.16	8.21
6	13.82	12.56	13.16	8.61

Appendix Va: Effect of Variation in Rate Parameters for
Disproportionation Process

1) Temperature 300 K

	Normal Value	Transition State Dissociation	Transition State Disproportionation
$\Delta E(\text{kJ})$		34.7	7.95
Vibrations	12	6	11
Frequencies cm^{-1}	100, 450, 450, 500 500, 800, 800, 800 1300, 1300, 3600 3600	1120, 1120, 1360 1360, 3400, 3400	100, 100, 500, 500* 700, 800, 800, 1300 1300, 3600, 3600
Active (1-d)	0	1(.5E-40) (a)	0
Rotors (2-d)	0	2(6.25E-78)	
Inactive (1-d)	1(6E-39) (a)	1(6E-39) (a)	1(6E-39) (a)
Rotors (2-d)	1(13E-39)	$I^+/I = 4.28$	1(13E-39)
α		.015	1
β		-2	0

(a) \overline{I} (gm-cm^2)
rotors

$$k(\text{diss})_{\infty} = 10^{15.7} \exp(-3923/T) \quad k_{\infty}(\text{assc}) = 9.28$$

$$k(\text{disp})_{\infty} = 10^{13.65} \exp(-1332/T)$$

LGT[P(torr)]	LGT[k(diss)/sec]	LGT[k(disp)/sec]	LGT[k(stab)/sec]	LGT[k(obs)l/mol-sec]
0	13.78	13.08	7.16	8.50
1	13.78	13.08	8.16	8.50
2	13.78	13.08	9.16	8.50
3	13.78	13.08	10.16	8.50
4	13.79	13.08	11.16	8.50
5	13.79	13.08	12.16	8.53
6	13.85	13.09	13.16	8.72

* changed from previous trial.

2) Temperature 300 K

	Normal Value	Transition State Dissociation		Transition State Disproportionation	
$\Delta E(kJ/s)$		34.7		7.95	
Vibrations	12	6		11	
Frequencies cm^{-1}	100, 450, 450, 500 500, 800, 800, 800 1300, 1300, 3600 3600	1120, 1120, 1360 1360, 3400, 3400		100, 100, 200, 200* 200, 200, 200, 1300 1300, 3600, 3600	
Active (1-d)	0	1(.5E-40)	(a)	0	(a)
Rotors (2-d)	0	2(6.25E-78)		0	
Inactive (1-d)	1(6E-39)	(a)	1(6E-39)	1(6E-39)	(a)
Rotors (2-d)	1(13E-39)		$I^+/I = 4.28$	1(13E-39)	
α		.015		1	
β		-2		0	

(a) \overline{I} (qm-cm²)
rotors

$$k(diss)_{\infty} = 10^{15.7} \exp(-3923/T) \quad k_{\infty}(assc) = 9.28$$

$$k(disp)_{\infty} = 10^{15.65} \exp(-1995/T)$$

LGT[P(torr)]	LGT[k(diss)/sec]	LGT[k(disp)/sec]	LGT[k(stab)/sec]	LGT[k(obs)l/mol-sec]
0	13.96	14.82	7.16	9.22
1	13.96	14.82	8.16	9.22
2	13.96	14.82	9.16	9.22
3	13.96	14.82	10.16	9.22
4	13.96	14.82	11.16	9.22
5	13.96	14.82	12.16	9.22
6	13.96	14.82	13.16	9.22

* changed from previous trial.

3) Temperature 300 K

	Normal Value	Transition State Dissociation		Transition State Disproportionation	
$\Delta E(\text{kJ/s})$		34.7		16.3*	
Vibrations	12	6		11	
Frequencies cm^{-1}	100, 450, 450, 500 500, 800, 800, 800 1300, 1300, 3600 3600	1120, 1120, 1360 1360, 3400, 3400		100, 100, 200, 200 200, 200, 200, 1300 1300, 3600, 3600	
Active (1-d)	0	1(.5E-40)	(a)	0	
Rotors (2-d)	0	2(6.25E-78)		0	
Inactive (1-d)	1(6E-39)	(a)	1(6E-39)	1(6E-39)	(a)
Rotors (2-d)	1(13E-39)		$I^+/I = 4.28$	1(13E-39)	
α		.015		1	
β		-2		0	

(a) \overline{I} (gm-cm^2)
rotors

$$k(\text{diss})_{\infty} = 10^{15.7} \exp(-3923/T) \quad k_{\infty}(\text{assc}) = 9.28$$

$$k(\text{disp})_{\infty} = 10^{15.65} \exp(-3002/T)$$

LGT[P(torr)]	LGT[k(diss)/sec]	LGT[k(disp)/sec]	LGT[k(stab)/sec]	LGT[k(obs)l/mol-sec]
0	13.87	14.07	7.16	9.06
1	13.87	14.07	8.16	9.06
2	13.87	14.07	9.16	9.06
3	13.87	14.07	10.16	9.06
4	13.87	14.07	11.16	9.06
5	13.87	14.07	12.16	9.07
6	13.89	14.07	13.16	9.08

* changed from previous trial.

4) Temperature 300 K

	Normal Value	Transition State Dissociation	Transition State Disproportionation
ΔE (kJ/s)		34.7	16.3
Vibrations	12	6	11
Frequencies cm ⁻¹	100, 450, 450, 500 500, 800, 800, 800 1300, 1300, 3600 3600	1120, 1120, 1360 1360, 3400, 3400	100, 100, 200, 200* 700, 800, 800, 1300 1300, 3600, 3600
Active (1-d)	0	1(.5E-40) (a)	0
Rotors (2-d)	0	2(6.25E-78)	0
Inactive (1-d)	1(6E-39) (a)	1(6E-39) (a)	1(6E-39) (a)
Rotors (2-d)	1(13E-39)	I ⁺ /I = 4.28	1(13E-39)
α		.015	1
β		-2	0

(a) \overline{I} (gm-cm²)
rotors

$$k(\text{diss})_{\infty} = 10^{15.7} \exp(-3923/T) \quad k_{\infty}(\text{assc}) = 9.28$$

$$k(\text{disp})_{\infty} = 10^{14.3} \exp(-2553/T)$$

LGT[P(torr)]	LGT[k(diss)/sec]	LGT[k(disp)/sec]	LGT[k(stab)/sec]	LGT[k(obs)l/mol-sec]
0	13.76	13.03	7.16	8.47
1	13.75	13.03	8.16	8.47
2	13.76	13.03	9.16	8.47
3	13.76	13.03	10.16	8.47
4	13.76	13.03	11.16	8.48
5	13.77	13.03	12.16	8.51
6	13.83	13.05	13.16	8.71

* changed from previous trial.

Appendix Vb: Effects Arising from Uncertainties in Thermochemistry of H_2O_4

Temperature 300 K

	Normal Value	Transition State Dissociation	Transition State Disproportionation
$\Delta E(kJs)$		55.64*	37.2*
Vibrations	12	6	11
Frequencies cm^{-1}	100, 450, 450, 500 500, 800, 800, 800 1300, 1300, 3600 3600	1120, 1120, 1360 1360, 3400, 3400	100, 100, 200, 200 700, 800, 800, 1300 1300, 3600, 3600
Active (1-d)	0	1(.5E-40) (a)	0
Rotors (2-d)	0	2(6.25E-78)	0
Inactive (1-d)	1(6E-39) (a)	1(6E-39) (a)	1(6E-39) (a)
Rotors (2-d)	1(13E-39)	$I^+/I = 4.93^*$	1(13E-39)
α		.015	1
β		-2	0

(a) \overline{I} (gm-cm²)
rotors

$$k(diss)_\infty = 10^{15.7} \exp(-6441/T) \quad k_\infty(assc) = 9.33$$

$$k(disc)_\infty = 10^{14.3} \exp(-5072/T)$$

LGT[P(torr)]	LGT[k(diss)/sec]	LGT[k(disp)/sec]	LGT[k(stab)/sec]	LGT[k(obs)%/mol-sec]
0	12.79	12.06	7.16	8.54
1	12.79	12.06	8.16	8.54
2	12.79	12.06	9.16	8.54
3	12.79	12.06	10.16	8.54
4	12.80	12.07	11.16	8.57
5	12.87	12.09	12.16	8.76
6	13.03	12.15	13.16	9.11

* changed from previous trial.

Appendix Vc: Effects Arising from Uncertainties in Vibrational
Frequencies for H_2O_4 complex

Temperature 300 K

	Normal Value	Transition State Dissociation	Transition State Disproportionation
$\Delta E(kJs)$		34.8*	7.95*
Vibrations	12	6	11
Frequencies cm^{-1}	100, 100, 100, 450 450, 450, 800, 800 1300, 1300, 3600 3600	1120, 1120, 1360 1360, 3400, 3400	100, 100, 500, 500* 700, 800, 800, 1300 1300, 3600, 3600
Active (1-d)	0	1(.5E-40) (a)	0
Rotors (2-d)	0	2(6.25E-78)	0
Inactive (1-d)	1(6E-39) (a)	1(6E-39) (a)	1(6E-39) (a)
Rotors (2-d)	1(13E-39)	$I^+/I = 4.28^*$	1(13E-39)
α		.006*	1
β		-2	0

(a) \overline{I} ($gm-cm^2$)
rotors

$$k(diss)_\infty = 10^{14.05} \exp(-3598/T) \quad k_\infty(assc) = 9.34$$

$$k(disps)_\infty = 10^{12.9} \exp(-1009/T)$$

LGT[P(torr)]	LGT[k(diss)/sec]	LGT[k(disps)/sec]	LGT[k(stab)/sec]	LGT[k(obs)l/mol-sec]
0	12.29	11.92	7.16	8.82
1	12.29	11.92	8.16	8.82
2	12.29	11.92	9.16	8.82
3	12.29	11.92	10.16	8.82
4	12.30	11.92	11.16	8.85
5	12.37	11.93	12.16	9.03
6	12.46	11.94	13.16	9.26

* changed from previous trial.

Appendix Vd: Effects arising from treatment of external rotations

Temperature 300 K

	Normal Value	Transition State Dissociation		Transition State Disproportionation	
$\Delta E(\text{kJ/s})$		34.8		7.95	
Vibrations	12	6		11	
Frequencies cm^{-1}	100, 100, 100, 450 450, 800, 800, 800 1300, 1300, 3600 3600	1120, 1120, 1360 1360, 3400, 3400		100, 100, 500, 500 700, 800, 800, 1300 1300, 3600, 3600	
Active (1-d)	1(6E-39)*	(a)	1(.5E-40)	(a)	0
Rotors (2-d)	0		2(6.25E-78)		0
Inactive (1-d)	0	*	1(6E-39)	(a)	1(6E-39)
Rotors (2-d)	1(13E-39)	(a)	$I^+/I = 4.28$		1(13E-39)
α			.006		1
β			-2		0

(a) \overline{I} (gm-cm²)
rotors

$$k(\text{diss})_{\infty} = 10^{14.05} \exp(-3599/T) \quad k_{\infty}(\text{assc}) = 9.34$$

$$k(\text{disp})_{\infty} = 10^{12.9} \exp(-1009/T)$$

LGT[P(torr)]	LGT[k(diss)/sec]	LGT[k(disp)/sec]	LGT[k(stab)/sec]	LGT[k(obs)&/mol-sec]
0	10.49	10.12	7.16	8.81
1	10.49	10.12	8.16	8.81
2	10.50	10.12	9.16	8.84
3	10.55	10.12	10.16	8.98
4	10.63	10.13	11.16	9.23
5	10.67	10.13	12.16	9.33
6	10.68	10.13	13.16	9.34

* changed from previous trial.

Appendix Ve: Effects arising from uncertainty in internal temperature of
H₂O₄ complex

1) Temperature 300 K [Internal temperature: 100 K]*

	Normal Value	Transition State Dissociation	Transition State Disproportionation
$\Delta E(kJs)$		34.8	7.95
Vibrations	12	6	11
Frequencies cm ⁻¹	100, 100, 400, 450 450, 800, 800, 800 1300, 1300, 3600 3600	1120, 1120, 1360 1360, 3400, 3400	100, 100, 500, 500 700, 800, 800, 1300 1300, 3600, 3600
Active (1-d)	1(6E-39)	(a) 1(.5E-40)	(a) 0
Rotors (2-d)	0	2(6.25E-78)	0
Inactive (1-d)	0	(a) 1(6E-39)	(a) 1(6E-39)
Rotors (2-d)	1(13E-39)	I ⁺ /I = 4.28	1(13E-39)
α		.006	1
β		-2	0

(a) \overline{I} (gm-cm²)
rotors

$$k(diss)_{\infty} = 10^{14.05} \exp(-3599/T) \quad k_{\infty}(assc) = 9.34$$

$$k(disp)_{\infty} = 10^{12.7} \exp(-1009/T)$$

LGT[P(torr)]	LGT[k(diss)/sec]	LGT[k(disp)/sec]	LGT[k(stab)/sec]	LGT[k(obs)l/mol-sec]
0	9.78	10.09	7.16	9.17
1	9.78	10.09	8.16	9.17
2	9.79	10.09	9.16	9.18
3	9.84	10.09	10.16	9.24
4	9.91	10.10	11.16	9.32
5	9.93	10.10	12.16	9.34
6	9.93	10.10	13.16	9.34

* changed from previous trial.

2) Temperature 300 K [Internal temperature: 100 K]

	Normal Value	Transition State Dissociation		Transition State Disproportionation	
$\Delta E(\text{kJ})$		34.8		7.95	
Vibrations	12	6		11	
Frequencies cm^{-1}	100, 100, 100, 450 450, 800, 800, 800 1300, 1300, 3600 3600	1120, 1120, 1360 1360, 3400, 3400		500, 500, 700, 700* 700, 800, 800, 1300 1300, 3600, 3600	
Active (1-d)	1(6E-39)	(a)	1(.5E-40)	(a)	0
Rotors (2-d)	0		2(6.25E-78)		0
Inactive (1-d)	0	(a)	1(6E-39)	(a)	1(6E-39)
Rotors (2-d)	1(13E-39)		$I^+/I = 4.28$		1(13E-39)
α			.006		1
β			-2		0

(a) \overline{I} (gm-cm²)
rotors

$$k(\text{diss})_{\infty} = 10^{14.05} \exp(-3599/T) \quad k_{\infty}(\text{assc}) = 9.34$$

$$k(\text{disp})_{\infty} = 10^{11.05} \exp(-614/T)$$

LGT[P(torr)]	LGT[k(diss)/sec]	LGT[k(disp)/sec]	LGT[k(stab)/sec]	LGT[k(obs)l/mol-sec]
0	9.51	8.82	7.16	8.58
1	9.52	8.82	8.16	8.63
2	9.62	8.82	9.16	8.86
3	9.80	8.82	10.16	9.19
4	9.90	8.82	11.16	9.33
5	9.93	8.82	12.16	9.34
6	9.93	8.82	13.16	9.34

* changed from previous trial.

Appendix VI: Inputs and Results for RRKM calculations for
 $\text{HO}_2 + \text{OH} \rightarrow \text{H}_2\text{O} + \text{O}_2$

Temperature 300 K Mass 50.016 Collision diameter 5 Å

	Normal Value	Transition State Dissociation	Transition State Disproportionation
$\Delta E(\text{kJ})$		97.9	65.3
Vibrations	9	4	8
Frequencies cm^{-1}	100, 100, 500 800, 800, 1300 1300, 3600, 3600	1100, 1400, 3400 3700	200, 200, 300, 300 1300, 1300, 3600 3600
Active (1-d)	0	(a) 2(1.2E-80)	(a) 0
Rotors (2-d)	0	1(2.5E-39)	0
Inactive (1-d)	1(1.7E-39)	(a) 1(1.7E-39)	(a) 1(1.7E-39)
Rotors (2-d)	1(9E-39)	$I^+/I = 5.89$	1(9E-39)
α		.22	1
β		-1.5	0

(a) \overline{I} (gm-cm²)
rotors

$$k(\text{diss})_{\infty} = 10^{15.35} \exp(-11551/T) \text{sec}^{-1} \quad k_{\infty}(\text{assc}) 10.8$$

$$k(\text{disp})_{\infty} = 10^{13.0} \exp(-8194/T) \text{sec}^{-1}$$

LGT[P(torr)]	LGT[k(diss)/sec]	LGT[k(disp)/sec]	LGT[k(stab)/sec]	LGT[k(obs)&/mol-sec]
0	11.63	11.19	7.15	10.23
1	11.63	11.19	8.15	10.23
2	11.63	11.19	9.15	10.23
3	11.64	11.20	10.15	10.25
4	11.69	11.21	11.15	10.38
5	11.83	11.24	12.15	10.64
6	11.91	11.26	13.15	10.78

Appendix VIb: Effects Arising from Uncertainties in Rate
Parameters for Disproportionation Process

Temperature 300 K

	Normal Value	Transition State Dissociation	Transition State Disproportionation
$\Delta E(\text{kJ/s})$		97.9	73.6*
Vibrations	9	4	8
Frequencies cm^{-1}	100, 100, 500 800, 800, 1300 1300, 3600, 3600	1100, 1400, 3400 3750	100, 200, 200, 300* 1300, 1300, 3600 3600
Active (1-d)	0	(a) 2(1.2E-80)	(a) 0
Rotors (2-d)	0	1(2.5E-39)	0
Inactive (1-d)	1(1.7E-39)	(a) 1(1.7E-39)	(a) 1(1.7E-39)
Rotors (2-d)	1(9E-39)	$I^+/I = 5.89$	1(9E-39)
α		.22	1
β		-1.5	0

(a) \overline{I} (gm-cm^2)
rotors

$$k(\text{diss})_{\infty} = 10^{15.35} \exp(-11551/T) \text{sec}^{-1} \quad k_{\infty}(\text{assc}) 10.8$$

$$k(\text{disp})_{\infty} = 10^{13.5} \exp(-9301/T) \text{sec}^{-1}$$

LGT[P(torr)]	LGT[k(diss)/sec]	LGT[k(disp)/sec]	LGT[k(stab)/sec]	LGT[k(obs)/mol-sec]
0	11.61	11.17	7.15	10.23
1	11.61	11.17	8.15	10.23
2	11.61	11.17	9.15	10.23
3	11.62	11.18	10.15	10.25
4	11.68	11.19	11.15	10.38
5	11.82	11.24	12.15	10.65
6	11.92	11.27	13.15	10.78

* changed from previous trial.

Appendix VIb: Effects Arising from Treatment of External Rotations

1) Temperature 300 K

	Normal Value	Transition State Dissociation	Transition State Disproportionation
$\Delta E(\text{kJ})$		97.9	73.6
Vibrations	9	4	8
Frequencies cm^{-1}	100, 100, 500 800, 800, 1300 1300, 3600, 3600	1100, 1400, 3400 3750	100, 200, 200, 300 1300, 1300, 3600 3600
Active (1-d)	1(1.7E-39)* (a)	2(1.2E-80) (a)	0
Rotors (2-d)	0	1(2.5E-39)	0
Inactive (1-d)	0 *	1(1.7E-39) (a)	1(1.7E-39) (a)
Rotors (2-d)	1(9E-39)	1 ⁺ /I = 5.89	1(9E-39)
α		.22	1
β		-1.5	0

(a) \overline{I} (gm-cm²)
rotors

$$k(\text{diss})_{\infty} = 10^{15.35} \exp(-11551/T) \text{sec}^{-1} \quad k_{\infty}(\text{assc}) 10.8$$

$$k(\text{disp})_{\infty} = 10^{13.5} \exp(-9301/T) \text{sec}^{-1}$$

LGT[P(torr)]	LGT[k(diss)/sec]	LGT[k(disp)/sec]	LGT[k(stab)/sec]	LGT[k(obs)l/mol-sec]
0	9.89	9.44	7.15	10.22
1	9.90	9.44	8.15	10.23
2	9.93	9.45	9.15	10.32
3	10.06	9.49	10.15	10.58
4	10.17	9.53	11.15	10.76
5	10.20	9.54	12.15	10.80
6	10.20	9.54	13.15	10.80

* changed from previous trial.

2) Temperature 300 K

	Normal Value	Transition State Dissociation	Transition State Disproportionation
$\Delta E(\text{kJ/s})$		97.9	73.6
Vibrations	9	4	8
Frequencies cm^{-1}	100, 100, 500 800, 800, 1300 1300, 3600, 3600	1100, 1400, 3400 3750	100, 160, 200, 300* 1300, 1300, 3600 3600
Active (1-d)	1(1.7E-39) (a)	3(2.04E-119)* (a)	1(1.7E-39) (a)
Rotors (2-d)	0	1(2.5E-39)	0
Inactive (1-d)	0 (a)	0 *	0
Rotors (2-d)	1(9E-39)	$I^+/I = 5.89$	1(9E-39) (a)
α		.22	1
β		-1.5	0

(a) \overline{I} (gm-cm^2)
rotors

$$k(\text{diss})_{\infty} = 10^{15.35} \exp(-11551/T) \text{sec}^{-1} \quad k_{\infty}(\text{assc}) 10.8$$

$$k(\text{disp})_{\infty} = 10^{13.6} \exp(-9322/T) \text{sec}^{-1}$$

LGT[P(torr)]	LGT[k(diss)/sec]	LGT[k(disp)/sec]	LGT[k(stab)/sec]	LGT[k(obs) l/mol-sec]
0	11.50	11.00	7.15	10.18
1	11.51	11.00	8.15	10.18
2	11.51	11.00	9.15	10.18
3	11.52	11.00	10.15	10.21
4	11.62	11.03	11.15	10.38
5	11.80	11.09	12.15	10.65
6	11.91	11.13	13.15	10.70

* changed from previous trial.

Appendix VIc: Effects Arising from Uncertainty in Thermochemistry

Temperature 300 K

	Normal Value	Transition State Dissociation	Transition State Disproportionation
$\Delta E(\text{kJ})$		118.8*	79.5*
Vibrations	9	4	8
Frequencies cm^{-1}	100, 100, 500 800, 800, 1300 1300, 3600, 3600	1100, 1400, 3400 3700	300, 300, 300, 300 1300, 1300, 3600 3600
Active (1-d)	0 *	2(1.2E-80)*	0
Rotors (2-d)	0	1(2.5E-39)	0
Inactive (1-d)	1(1.7E-39)* (a)	1(1.7E-39)* (a)	1(1.7E-39) (a)
Rotors (2-d)	1(9E-39)	$I^+/I = 6.26$	1(9E-39)
α		.22	1
β		-1.5	0

(a) \bar{I} (gm-cm²)
rotors

$$k(\text{diss})_{\infty} = 10^{15.4} \exp(-14070/T) \text{sec}^{-1} \quad k_{\infty}(\text{assc}) 10.83$$

$$k(\text{disp})_{\infty} = 10^{12.7} \exp(-9818/T) \text{sec}^{-1}$$

LGT[P(torr)]	LGT[k(diss)/sec]	LGT[k(disp)/sec]	LGT[k(stab)/sec]	LGT[k(obs)l/mol-sec]
0	11.22	10.76	7.15	10.25
1	11.22	10.76	8.15	10.25
2	11.22	10.76	9.15	10.26
3	11.22	10.76	10.15	10.31
4	11.32	10.78	11.15	10.52
5	11.46	10.81	12.15	10.75
6	11.51	10.82	13.15	10.82

* changed from previous trial.

Appendix VI d: Effects Due to Changes in Frequencies of Molecule

Temperature 300 K

	Normal Value	Transition State Dissociation	Transition State Disproportionation
$\Delta E(\text{kJ/s})$		118.8	66.94*
Vibrations	9	4	8
Frequencies cm^{-1}	500, 500, 500* 800, 800, 1300 1300, 3600, 3600	1100, 1400, 3400 3700	300, 300, 300, 300 1300, 1300, 3600 3600
Active (1-d)	0	2(1.2E-80) (a)	0
Rotors (2-d)	0	1(2.5E-39)	0
Inactive (1-d)	1(1.7E-39) (a)	1(1.7E-39) (a)	1(1.7E-39) (a)
Rotors (2-d)	1(9E-39)	$I^+/I = 6.26$	1(9E-39)
α		.6*	1
β		-1.5	0

(a) \overline{I} (gm-cm^2)
rotors

$$k(\text{diss})_{\infty} = 10^{17} \exp(-14394/T) \text{sec}^{-1} \quad k_{\infty}(\text{assc}) 10.80$$

$$k(\text{disp})_{\infty} = 10^{13.95} \exp(-8630/T) \text{sec}^{-1}$$

LGT[P(torr)]	LGT[k(diss)/sec]	LGT[k(disp)/sec]	LGT[k(stab)/sec]	LGT[k(obs)g/mol-sec]
0	12.95	12.54	7.15	10.24
1	12.95	12.54	8.15	10.24
2	12.95	12.54	9.15	10.24
3	12.95	12.54	10.15	10.25
4	12.96	12.54	11.15	10.25
5	12.99	12.54	12.15	10.33
6	13.10	12.56	13.15	10.57

* changed from previous trial.

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